DETERMINATION OF COBALT, COPPER, LEAD AND NICKEL IN GYPSUM BY ZEEMAN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract

A rapid method was developed for the extraction of cobalt, copper, lead and nickel from dissolved mineral samples by sodium diethildithiocarbamate into methylisobutyl ketone and their determination by Zeeman electrothermal atomic absorption spectrometry. The matrix interferences were investigated and results show that Ca (as matrix element) tends to decrease absorbance of investigated elements. Therefore, a separation of Co, Cu, Pb and Ni from the solution obtained by dissolution of gypsum in HCl was suggested. Standard addition technique was used for the evaluation of data and the method was tested using certified reference materials. The standard deviation (*s*) is 4 $ng \cdot g^{-1}$ for Co, 17 $ng \cdot g^{-1}$ for Cu, 8 $ng \cdot g^{-1}$ for Pb and 7 $ng \cdot g^{-1}$ for Ni. The detection limit of the method, calculated as 3*s* of the blank, was found to be 12 $ng \cdot g^{-1}$ for Co, 51 $ng \cdot g^{-1}$ for Cu, 24 $ng \cdot g^{-1}$ for Pb and 21 $ng \cdot g^{-1}$ for Ni.

Introduction

By the definition a minerals are naturally occurring inorganic substances having a relatively constant chemical composition. Beside that, it must always be borne in mind that this does not mean they are chemically pure substances. Namely, that most of minerals contain extraneous substances, and these often change their characteristics. In the other side, the knowledge about the presence of trace elements in the mineral sample helps to establish the condition in which these minerals had been formed. Gypsum, $CaSO_4 \cdot 2H_2O$, is wide spread mineral. In nature gypsum crystallizes in simple prism crystals. Sometimes crystals of gypsum have different colors depending of the presence of extraneous substances. Gypsum is a mineral that is used in different industries (construction, chemistry etc.). Therefore, it is very important to follow the content of trace elements in samples of gypsum.

The graphite furnace technique of atomic absorption spectrometry has proved to be very useful in geological analysis. The first investigations for the determination of Co, Cu,

Pb and Ni in geological samples with calcium matrix by atomic absorption spectrometry (AAS) refer to the application of flame AAS. Many authors suggest directly determination by flame or electrothermal AAS from the obtained solutions[1-5] or in the cases when the calcium is present in higher concentration, matrix modification or separation was suggested.[6-12] Thus, Manning and Slavin suggest matrix modification and molybdenum coating of the pyrolytically coated graphite tubes for lead determination in the presence of higher concentrations of calcium.[6] Matrix modifier is suggested in the analysis of investigated elements without preconcentration[7]. Also, separation methods are suggested using ion exchange after complex sample preparation procedure,[8] or by extraction with different complexes.[9-12]

In this work we proposed a method for determination of cobalt, copper, lead and nickel in gypsum using Zeeman electrothermal atomic absorption spectrometry (ETAAS) after an extraction of these elements by sodium diethyldithiocarbamate in methylisobutyl ketone (MIBK).

Experimental

Apparatus

A Varian SpectrAA-604Z Zeeman atomic absorption spectrophotometer equipped with a Varian PSD-100 Autosampler was used. A hollow cathode lamp was used as a source. The instrumental parameters are given in Table I.

Reagents and samples

All reagents were of analytical grade. Stock solutions of cobalt, copper, lead and nickel were prepared by dissolving $CoCl_2$, $CuCl_2$, $Pb(NO_3)_2$ and $NiCl_2$ in redistilled water. The concentration of cobalt, copper, lead and nickel in these solutions were 1 mg/ml, from which all diluted solutions were prepared.

Samples of gypsum minerals originate from two mines from Republic of Macedonia (Debar and Delcevo).

Table 1. Instrumental parameters for determination of Co, Ni, Cu and Pb by ETAAS

Parameters	Co	Ni	Cu	Pb
Wavelength, nm	242.5	232.0	327.4	283.3
Slit, nm	0.2	0.2	0.5	0.5
Lamp current, mA	7.0	4.0	4.0	5.0
Calibration mode	Absorbance, peak height			
Background correction	Zeeman			
DRY				
Temperature, °C	120	120	90	90
Ramp Time, s	55	55	35.0	35.0
Hold time, s	-	-	-	-
PYROLYSIS				
Temperature, °C	400	800	700	200
Ramp Time, s	5	10	5	5
Hold time, s	22	22	22	22
ATOMIZE				
Temperature, °C	2300	2400	2300	2100
Ramp Time, s	1	1	1	1
Hold time, s	2	2	2	2
CLEAN				
Temperature, °C	2650	2650	2560	2560
Ramp Time, s	5	5	5	5
Hold time, s	-	-	-	-
GAS	Argon			

Procedure

0.1 to 0.5 g of powdered sample of gypsum was dissolved in a mixture of concentrated HCl and concentrated HNO_3 (5+1). A few drops of H_2O_2 were added and the solution evaporated to near dryness. The residue was dissolved in 2 ml of concentrated HCl and 13 ml redistilled water was added. The solution was transferred into a separatory funnel. 5 ml of ammonium citrate (50 % w/v) were added and the pH value was adjusted with NaOH (20 %) to 6. Then, 5 ml of sodium diethyldithiocarbamate (0.2 %) were added and the mixture was shaken for 1 min. After 15 min, 5 ml of MIBK were added and the mixture was shaken for 2 min. Cobalt, copper, lead and nickel were determinate by ETAAS in the organic layer.

Results and Discussion

As mentioned above, the major problem, which must be confronted in electrothermal AAS, besides the choice of appropriate instrumental parameters, regards the study and control of the matrix effects. The interference of matrix element of the mineral studied (Ca) on the cobalt, copper, lead and nickel determination was investigated. Series of solutions with the same concentration of these elements and different concentration of calcium were prepared so that their mass ratios were similar to the ratios in the sample solutions.

Results show that calcium tend to decrease the absorbance of Co, Cu, Pb and Ni at high concentration (Figure 1). Due to the low concentrations of the investigated elements in the sample, it is necessary to separate and concentrate cobalt, copper, lead and nickel from gypsum. For this reason, an extraction method is proposed.

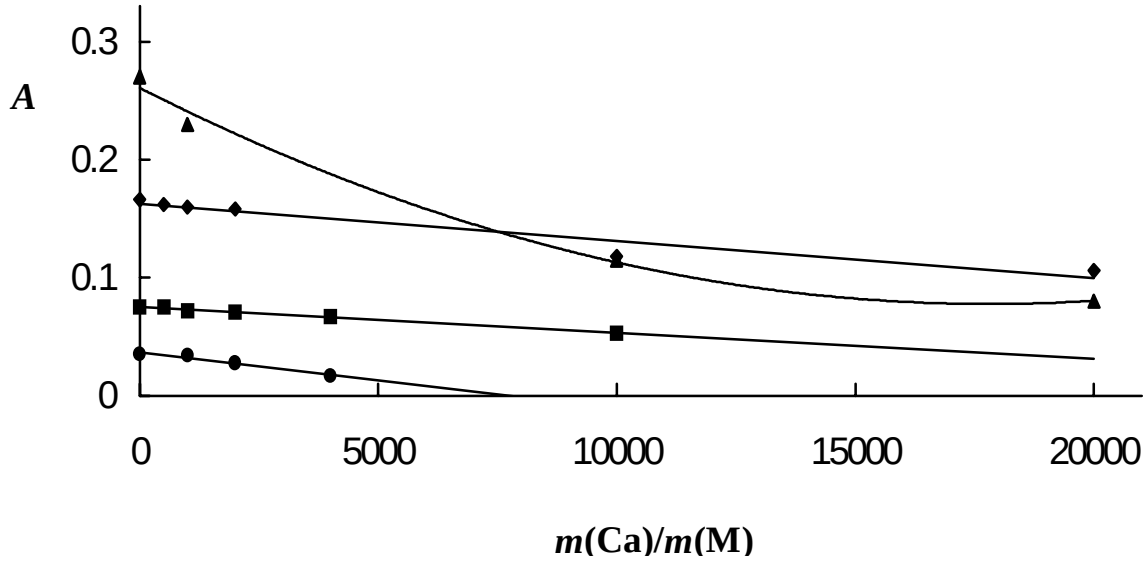
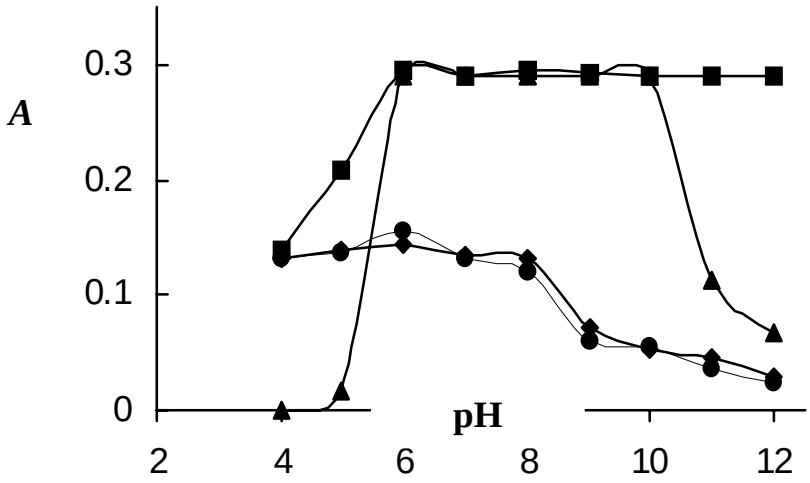


Figure. 1. Influence of Ca as matrix element on Co (◆), Cu (■), Pb (▲) and Ni (●) absorbance

Bode[13] found that Co, Cu, Pb and Ni could be satisfactorily extracted with sodium dithiocarbamate in CCl_4 in the pH region of 5-11. He found that this extraction is better when ammonium citrate and KCN are added. We found that the extraction of these elements with sodium diethyldithiocarbamate can be performed without KCN addition

using MIBK as an solvent, in the pH range 6-12 for copper, 6-10 for Pb and pH 6 for cobalt and nickel (Figure 2).

Figure 2. Influence of pH of inorganic phase on Co (◆), Cu (■), Pb (▲) and Ni (●)



absorbance

To check whether Ca coextract with investigated elements, a series of solutions with the same concentrations of interfering element were prepared and Co, Cu, Pb and Ni were extracted by the proposed procedure with MIBK. After the extraction these elements were determined in the organic phase and no interferences on their absorbance were found. Also, aliquot of organic layer was separated, evaporated to dryness and the residue dissolved in 2 cm^3 of conc. HCl. Using flame AAS, it was found that extracted amounts of the Ca was in range that have not any effect on the absorbance of the investigated elements.

Using this method some samples of the investigated mineral taken from two mines from the Republic of Macedonia, were extracted and Co, Cu, Pb and Ni were determined (with and without standard additions). Results given in Table 2 show that satisfactory recovery (*R*) results were obtained.

Table 2. Determination of cobalt, copper, lead and nickel in gypsum by method of standard addition

Sample	w_M(added)/ng·g^{-1}	w(calc.)/ng·g^{-1}	w(found)/ng·g^{-1}	R/%
Co				
Gypsum, Delcevo	-	-	25.6	-
	99.7	125.3	135.6	108.2
	200.0	225.6	225.5	100.0
	497.0	522.6	517.9	99.1
	994.0	1019.6	1014.9	99.5
Gypsum, Debar	-	-	43.7	-
	99.4	143.1	143.6	100.3
	199.4	243.1	243.8	100.2
	498.0	541.7	547.8	101.1
	993.0	1036.7	1029.8	99.3
Cu				
Gypsum, Delcevo	-	-	145.4	-
	99.1	244.6	252.3	103.1
	198.8	344.2	344.4	100.1
	496.0	641.4	654.3	102.0
	985.2	1130.6	1152.7	101.9
Gypsum Debar	-	-	151.4	-
	99.8	251.2	251.6	100.2
	199.2	350.6	349.9	99.8
	496.0	647.4	674.6	104.1
Pb				
Gypsum, Delcevo	-	-	174.2	-
	99.8	274.0	291.9	106.5
	198.2	372.4	371.2	99.7
	497.0	671.2	657.1	97.9
Gypsum, Debar	-	-	136.6	-
	99.7	236.3	235.6	99.7
	199.0	335.6	333.3	99.3
	492.6	629.2	625.3	99.4
Ni				
Gypsum, Delcevo	-	-	43.3	-
	99.7	143.0	147.2	102.9
	198.8	242.1	242.1	100.0
	497.0	540.3	548.1	101.4

Determination of cobalt, nickel and lead were also performed for some certified reference materials. The results of measured and certified values of examined elements for these certified reference materials are given in Table 3. As it can be seen, the content

for cobalt, nickel, lead and copper obtained using the proposed methods are very similar to the certified values.

Table 3. Determination of Co, Ni and Pb in referent standards samples (given in %)

Certified reference materials	Co		Ni		Pb		Cu	
	Certified	Found	Certified	Found	Certified	Found	Certified	Found
Su-1	0.063	0.084± 0.002	1.51	1.46± 0.04	0.01	0.011± 0.002	-	-
Su-1a	0.041± 0.001	0.040± 0.001	1.233± 0.008	1.040± 0.010	-	-	-	-
UM-1	0.035	0.037± 0.002	0.88	0.95± 0.008	-	-	-	-
NR-3	0.074	0.084± 0.005	0.04	0.040± 0.002	-	-	-	-
JSS 820-2	-	-	-	-	-	-	0.001± 0.0002	0.001± 0.0002
JSS 830-3	-	-	-	-	-	-	0.011± 0.001	0.011± 0.003

Evaluation of results was performed applying standard addition technique. The standard deviation (*s*) is 4 $ng \cdot g^{-1}$ for Co, 17 $ng \cdot g^{-1}$ for Cu, 8 $ng \cdot g^{-1}$ for Pb and 7 $ng \cdot g^{-1}$ for Ni. The detection limit of the method, calculated as 3 *s* of the blank, was found to be 12 $ng \cdot g^{-1}$ for Co, 51 $ng \cdot g^{-1}$ for Cu, 24 $ng \cdot g^{-1}$ for Pb and 21 $ng \cdot g^{-1}$ for Ni.

Conclusion

It was shown that MIBK could be successfully applied for cobalt, copper, lead and nickel extraction from sulfate minerals as diethyldithiocarbamate complexes. The method of Zeeman electrothermal atomic absorption spectrometry was used for determination of investigated elements. The advantage of the proposed method compared with to other established method is the possibility of simple and simultaneously extraction and concentration of Co, Cu, Ni and Pb from calcium matrix. Therefore this method gave the possibility to obtained very low detection limits for all investigated elements.

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Povzetek

Razvili smo hitro metodo za ekstrakcijo kobalta, bakra, svinca in niklja iz raztopin mineralov z natrijevim dietilditiokarbamatom v metil izobutil keton in njihovo določitvijo z Zeeman ovo elektrotermičn o atomsko absorpcijsko spektrometrijo. Raziskali smo vpliv matriksa in ugotovili, da kalcij (kot element matriksa) zmanjša absorbance prisotnih elemen tov. Zato predlagamo ločitev Co, Cu, Pb in Ni z raztapljanjem sadre v HCl. Za evalvacijo rezultatov smo uporabili metode stan dardn ega dodatka in referen čn ih materialov.

Standardne deviacije (s) so bile 4 $ng \cdot g^{-1}$ za Co, 17 $ng \cdot g^{-1}$ za Cu, 8 $ng \cdot g^{-1}$ za Pb, in 7 $ng \cdot g^{-1}$ za Ni. Meja detekcije metode, izračunana kot 3*s* slepe probe, je 12 $ng \cdot g^{-1}$ za Co, 51 $ng \cdot g^{-1}$ za Cu, 24 $ng \cdot g^{-1}$ za Pb in 21 $ng \cdot g^{-1}$ za Ni.